Theoretical Studies on Condensed Phase Dynamics

Department of Theoretical and Computational Molecular Science
Division of Computational Molecular Science

SAITO, Shinji	Professor
KIM, Kang	Assistant Professor
HIGASHI, Masahiro	JSPS Post-Doctoral Felloww
YAGASAKI, Takuma	Post-Doctoral Fellow
IMOTO, Sho	Graduate Student
KAWAGUCHI, Ritsuko	Secretary

Liquids and biological systems show complicated dynamics because of their structural flexibility and dynamical hierarchy. Understanding these complicated dynamics is indispensable to elucidate chemical reactions and relaxation in solutions and functions of proteins. We have been investigating complex dynamics in supercooled liquids,[1–3] chemical reactions in biological systems using molecular dynamics simulation[4] and the stability of ions at water/vapor interface.[5] In addition, we have been theoretically investigating liquid dynamics by using linear and higher-order nonlinear IR spectroscopy.[6,7]

1. Role of the Lifetime of Dynamical Heterogeneity in the Frequency-Dependent Stokes–Einstein Relation of Supercooled Liquids[1]

We previously investigated the lifetime of dynamical heterogeneity in supercooled liquids in terms of a four-point, three-time density correlation function *via* molecular dynamics simulations [*Phys. Rev. E* **79**, 060501(R) (2009); *J. Chem. Phys.* **133**, 044511 (2010)]. In this letter, we examine the physical role of the lifetime of dynamicsl heterogeneity in the violation of the Stokes–Einstein (SE) relation by calculating the frequency-dependent viscosity and self-diffusion constant. Our results demonstrate that the SE relation holds up to the time scale at which the non-Gaussian parameter is maximum. Large violations of the SE relation are characterized by time scales longer than the lifetime of the dynamical heterogeneity in highly supercooled liquids.

2. Hidden Slow Time Scale of Correlated Motions in Supercooled Liquids: Multi-Time Correlation Function Approach[2]

A three-time correlation function of particle displacements is introduced and numerically calculated by performing molecular dynamics simulations of binary soft-sphere supercooled systems. It is found that the two-dimensional representations of the three-time correlation function reveal couplings of particle motions that exist over a wide range of time scales. Furthermore, it is demonstrated that the systematic change in the second time interval in the three-time correlation function enables us to analyze how the correlations in mobility decay with time. From this analysis, the characteristic time scale of dynamical heterogeneity is quantified. We find that the dynamical heterogeneity time scale becomes much slower than the α-relaxation time as the temperature decreased.

3. Relation between Conformational Heterogeneity and Reaction Cycle of Ras: Molecular Simulation of Ras[4]

Ras functions as a molecular switch by cycling between the active GTP-bound state and the inactive GDP-bound state.

It is known experimentally that there is another GTP-bound state called state 1. We investigate the conformational changes and fluctuations arising from the difference in the coordinations between the switch regions and ligands in the GTP and GDP-bound states using a total of 830 ns of molecular-dynamics simulations. Our results suggest that the large fluctuations among multiple conformations of switch I in state 1 owing to the absence of coordination between Thr-35 and Mg^{2+} inhibit the binding of Ras to effectors. Furthermore, we elucidate the conformational heterogeneity in Ras by using principal component analysis, and propose a two-step reaction path from the GDP-bound state to the active GTP-bound state *via* state 1. This studysuggests that state 1 plays an important role in signal transduction as an intermediate state of the nucleotide exchange process, although state 1 itself is an inactive state for signal transduction.

4. Effects of Nonadditive Interactions on Ion Solvation at the Water/Vapor Interface: A Molecular Dynamics Study[5]

The solvation of halide ions at the water/vapor interface is investigated by using molecular dynamics simulations with nonpolarizable molecular mechanical (MM), polarizable MM, and quantum mechanical (QM)/MM methods. The free energy profile of the ion solvation is decomposed into the energy and the entropic contributions along the ion displacement from inside to the surface of water. It is found that the surface affinity of the ion, relative to the bulk value, is determined by a subtle balance between the energetic destabilization and the entropic stabilization with the ion displacement. The amount of energetic destabilization is found to be reduced when nonadditive interactions are included, as in the polarizable MM and QM/MM models. The structure of water around the ion at the interface is also largely modified when the higher order effects are considered. For example, the induced dipole effect enhances the solvation structure around the ion at the interface significantly and thus reduces the amount of entropic stabilization at the interface, relative to in the bulk. It is found that this induced dipole effect causes the slowing in the ion–water hydrogen bond dynamics at the interface. On the other hand, the higher order induced multipole effects in the QM/MM method suppress both the excessive enhancement of the solvation structure and the slowing of the ion–water hydrogen bond dynamics at the interface. The present study demonstrates that not only the induced dipole moment but also the higher order induced multipole moments, which are neglected in standard empirical models, are essential for the correct description of the ion solvation at the water/vapor interface.

5. A Novel Method for Analyzing Energy Relaxation in Condensed Phases Using Nonequilibrium Molecular Dynamics Simulations: Application to the Energy Relaxation of Intermolecular Motions in Liquid Water[6]

We present a novel method to investigate energy relaxation processes in condensed phases using nonequilibrium molecular dynamics simulations. This method can reveal details of the time evolution of energy relaxation like two-color third-order IR spectroscopy. Nonetheless, the computational cost of this method is significantly lower than that of third-order response functions. We apply this method to the energy relaxation of intermolecular motions in liquid water. We show that the intermolecular energy relaxation in water is characterized by four energy transfer processes. The structural changes of the liquid associated with the energy relaxation are also analyzed by the nonequilibrium molecular dynamics technique.

References

1) K. Kim and S. Saito, *J. Phys Soc. Jpn.* **79**, 093601 (4 pages) (2010).

2) K. Kim and S. Saito, *J. Non-Crys. Solids* **357**, 371–375 (2010).

3) K. Kim, K. Miyazaki and S. Saito, *Eur. Phys. J. Special Topics* **189**, 135–139 (2010).

4) C. Kobayashi and S. Saito, *Biophys. J.* **99**, 3726–3734 (2010).

5) T. Yagasaki, S. Saito and I. Ohmine, *J. Phys. Chem. A* **114**, 12573–12584 (2010). (invited)

6) T. Yagasaki and S. Saito, *J. Chem. Phys.* **134**, 184503 (9 pages) (2011).

7) S. Yamaguchi, S. Saito and K. Tominaga, *Phys. Chem. Chem. Phys.* **13**, 14742–14749 (2011).